

The effect of oxygen on the $\text{Ti}(\text{OBu})_4\text{—AlR}_3$ catalytic system in the dimerization of ethylene to 1-butene

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The effect of O_2 on the $\text{Ti}(\text{OBu})_4\text{—AlR}_3$ catalytic system in the dimerization of ethylene to 1-butene is studied. It is shown that O_2 readily interacts with excess AlR_3 and reduces the deactivating capability of trialkylaluminium, converting it into the less reactive AlR_2OR . The optimal conditions of the dimerization reaction in the presence of O_2 are found. An explanation of the effect of O_2 on the catalytic system is proposed.

Key words: titanium tetra-*n*-butoxide, triisobutylaluminium, dimerization, ethylene, hydrolysis, deuterioethane, isobutane.

Selective dimerization of ethylene in the presence of the $\text{Ti}(\text{OBu})_4\text{—AlEt}_3$ catalytic system is observed only for the molar ratio $\text{Al/Ti} > 1$ (see Ref. 1). When the co-catalyst is replaced with AlBu^i_3 , there is also a threshold ratio ($\text{Al/Ti} = 2.5$). Below this value, ethylene dimerization does not occur.² On the other hand, the rapid decrease in the dimerization rate (after the maximum value has been achieved) is known to be due to the interaction of the excess AlR_3 with the $\equiv\text{Ti—CH}_2\text{—CH}_2\text{—Ti}\equiv$ active centers (see Ref. 3). There are various methods for protecting the catalytic system from the excess co-catalyst.⁴ In this work, data on reducing the inhibiting action of the excess AlR_3 by oxygen additives, after the formation of the dimerization active centers, are presented.

Experimental

$\text{Ti}(\text{OBu})_4$ and AlBu^i_3 were purified by distillation *in vacuo* (the middle fraction was taken) and used as heptane solutions with concentrations of 10^{-3} mol mL^{-1} . Ethylene was purified by passing through a column filled with a 13X activated molecular sieve. Ethylene and heptane were purified from traces of oxygen by repeated freezing in liquid nitrogen and evacuating. The purity was checked by chromatography. The dimerization rate was monitored by the change in the ethylene pressure within the known volume, and the pressure over the catalytic mixture was maintained constant by a contact manometer coupled with a relay. Gaseous products were studied on a Tsvet-1 chromatograph. Mass spectra of products of the decomposition of the reaction mixture with heavy water were recorded on MI-1305 and MX-1302 instruments. The components of the mixture were preliminarily separated on a Tsvet-1

chromatograph. The compositions of the deuterioethanes were calculated according to the distribution of fission ions.⁵

Results and Discussion

To reduce the chemical activity of AlR_3 , O_2 is added to the catalytic system. Its interaction with trialkylaluminium results in the formation of AlR_2OR .⁶ Aluminium alkoxy-derivatives are known to be considerably less active in the reduction of titanates.⁷ In fact, although a large amount of oxygen added to the $\text{Ti}(\text{OBu})_4\text{—AlEt}_3$ catalytic system ($\text{O}_2 : \text{AlEt}_3 = 1 : 1$) results in decolorization of the solution and a decrease in its activity, the conditions can be found wherein the product yield considerably increases upon the addition of O_2 . It follows from Fig. 1 that a considerably greater amount of ethylene is absorbed in the presence of O_2 (curve 4) than that in its absence (curve 1). Increasing the amount of O_2 above the optimum results in a sharp decrease in the yield of the products (curve 2). This can be explained by the fact that high O_2 concentrations result in the interaction of O_2 not only with AlR_3 , but also with the Ti—C bonds of the active centers to cause their decay.

As can be seen from Fig. 2, the moment when oxygen is added to the system is also of great significance. When O_2 is added before the formation of active centers, it should, in fact, impede their formation, because some Al—R bonds are replaced with Al—OR bonds, and the reducing capability of the alkyl is decreased (there is a change in the Al/Ti molar ratio, which is of great significance for the choice of the

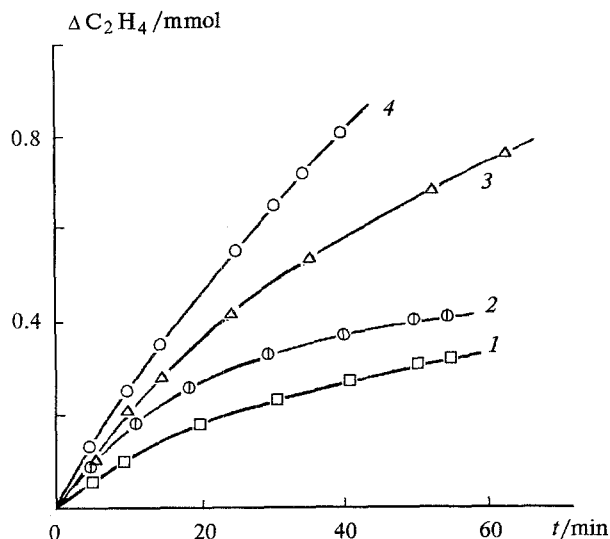


Fig. 1. Effect of oxygen on the kinetics of ethylene dimerization in the $\text{Ti}(\text{OBu})_4\text{--AlEt}_3$ system (1-butene as the solvent; $[\text{Ti}(\text{OBu})_4] = 5 \cdot 10^{-3} \text{ mol L}^{-1}$; $\text{Al/Ti} = 10$; 313 K; $p_{\text{tot}} = 1.5 \text{ MPa}$; $V = 0.2 \text{ L}$, added $\text{O}_2 \cdot 10^3 \text{ mol}$: 0 (1), 0.8 (2); 1.25 (3); 1.65 (4).

optimum conditions of dimerization). This results in a decrease in the number of the active centers and hence, in the maximum rate of the process (curve 1). The addition of O_2 at the stage of the formation of active centers can also result in a decrease in the number of active centers (curve 2) due to the interaction of ethylene with the reduced titanium derivatives (during the first 15–20 min). When O_2 is added after the formation of the active centers, the maximum rate is equal to the maximum dimerization rate when no O_2 has been added.

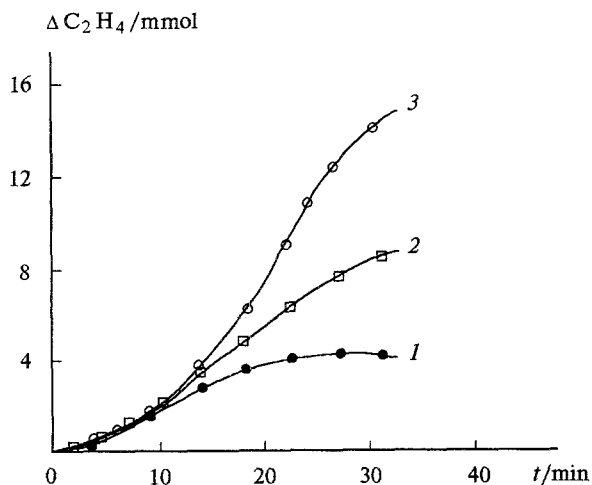
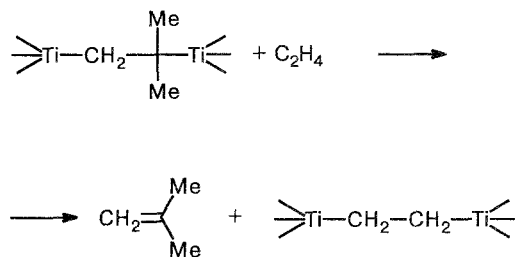


Fig. 2. Effect of the time of the addition of oxygen to the $\text{Ti}(\text{OBu})_4\text{--AlBu}_3$ catalytic system on the kinetics of ethylene dimerization ($[\text{Ti}(\text{OBu})_4] = 1.14 \cdot 10^{-2} \text{ mol L}^{-1}$; $\text{Al/Ti} = 7.5$; $p_{\text{C}_2\text{H}_4} = 3.4 \cdot 10^{-2} \text{ MPa}$; 293 K; 17.5 mL of heptane). 1–3, indicate the time of the addition of O_2 ($2.91 \cdot 10^{-4} \text{ mol}$): 0 (1); 5 min (2); 20 min (3).

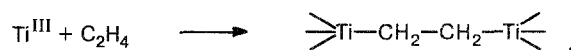
However, the further shape of the kinetic curve depends on the amount of O_2 added: excess O_2 results in a fast drop of the dimerization rate to zero due to the destruction of active centers as they react with O_2 . However, under optimum conditions, a high reaction rate is retained longer than in the blank experiment, as was mentioned above (see Fig. 1).

The products of the hydrolysis of the catalytic system were studied to reveal the mechanism of the effect of O_2 on the $\text{Ti}(\text{OBu})_4\text{--AlBu}_3$ system during ethylene dimerization.

It has previously been shown² that the S-like shape of the kinetic curve of ethylene absorption observed when AlEt_3 is replaced with AlBu_3 is associated with the formation of $\equiv\text{Ti--CH}_2\text{--CH}_2\text{--Ti}\equiv$ active centers according to the reaction:



or with oxidizing Ti^{III} derivatives by ethylene:¹



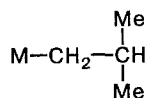
The formation of the active centers usually takes 15–20 min (see Fig. 2), during which time the total amount of hydrolysis gas (n) in the catalytic mixture changes (Table 1). After this time (15–20 min), the amount of hydrolysis gas is almost unchanged, which indicates the completion of the formation of active centers. The accumulation of various ethane isotopes in the hydroly-

Table 1. Dependence of the total amount of hydrolysis gas (n), and mono- and 1,2-dideuteroethanes on the duration of contact with C_2H_4

t/min	$n \cdot 10^3$	$\text{C}_2\text{H}_5\text{D}(\times 10^{-5})$	
		/mol	
5	2.10	0.57	0.08
8	1.57	0.71	0.16
14	1.32	0.82	0.20
18	1.20	—	—
20	1.25	0.92	0.22
30	1.15	0.99	0.22
40	1.20	1.04	0.23
50	1.20	1.09	0.22
70	1.20	1.20	0.23

Note. Conditions: $[\text{Ti}(\text{OBu})_4] = 1.4 \cdot 10^{-2} \text{ mol L}^{-1}$, $\text{Al/Ti} = 7.5$, $p_{\text{C}_2\text{H}_4} = 3.4 \cdot 10^{-2} \text{ MPa}$, $T = 293 \text{ K}$, 17.5 mL of heptane.

sis gas occurs during approximately the same time (see Table 1). Since during the hydrolysis of the catalytic system ethane isotopes can be produced from M—Et moieties formed *via* the replacement of isobutylene by ethane in



and from the M—CH₂—CH₂—M type products, which are active centers if both of metal atoms are titanium (M = Ti), the method of labeled atoms was used to separate these two ethane isotopes. Hydrolysis of the catalytic mixture by D₂O results in the formation of monodeuteroethane from the M—Et bonds and 1,2-dideuteroethane from the M—CH₂—CH₂—M type bonds. The amounts of these products were estimated from the mass spectral data. This estimation shows that only ~20 % of all ethane isotopes are formed from M—CH₂—CH₂—M (see Table 1), and this amount does not change with time. The addition of O₂ to the catalytic system and the subsequent hydrolysis never result in an increased content of ethane, and the efficiency of the catalyst is considerably higher than in the oxygen-free system. Depending on the amount of O₂ added, the total amount of gas formed in the hydrolysis (mainly, Buⁱ) decreases, which is related to the transformation of M—R to M—OR and the formation of the alcohol, whose vapor pressure is insignificant at room temperature, instead of the alkane during hydrolysis. When a large amount of O₂ is added to the system, the amount of ethane in the hydrolysis gas decreases. It is likely that the number of active centers also decreases due to their destruction by oxygen. The correlation between the amount of ethylene absorbed after 30 min and the amount of ethane found in the hydrolysis gases is shown in Fig. 3. A decrease in the amount of ethane formed in the hydrolysis caused by the excess O₂ results in a decrease in the yield of 1-butene. In addition to compounds of the M—Et type, *p*-Bu—M organometallic compounds, which produce *n*-butane after hydrolysis by water (reactions 1, 2), are accumulated over time in the dimerization of ethylene in the presence of Ti(OBu)₄—AlBuⁱ₃.



n-Butane is not formed in the insertion of ethylene into the Ti—C bond in the ≡Ti—CH₂—CH₂—Ti≡ active center, because the amount of mono- and dideuteroethane formed does not decrease (see Table 1). The normal

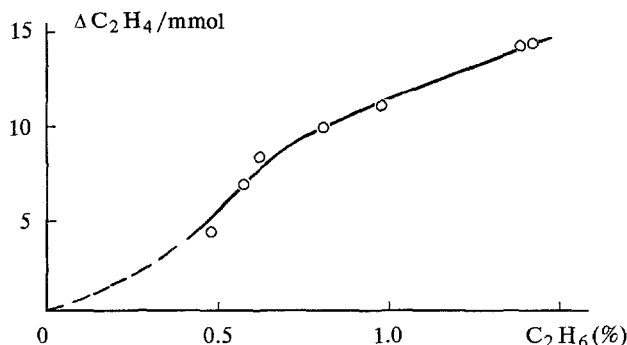
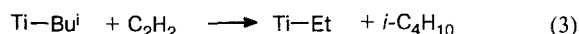


Fig. 3. Correlation between the yield of 1-butene and the amount of ethane in the hydrolysis gases for 30 min. For conditions see Fig. 2.

butyl radical is probably formed in the course of the insertion of ethylene into the Ti—Et bond formed due to the replacement of Buⁱ in the TiBuⁱ moiety under the action of ethylene (reaction 3).



Then the *n*-butyl group can transfer to Al *via* intermolecular radical exchange.

Thus, removing the excess trialkylaluminum from the subsequent reactions causes an increase in the 1-butene yield in the presence of optimum additives of O₂.

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